Ph.D. Synopsis submitted to

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"Studies on chemically synthesized Cu_2FeSnS_4 thin films"

For the Faculty of Science to be submitted in front of RRC

Abstract of proposed work plan/problem:

In present research work **Cu_2FeSnS_4**thin films will be deposited onto amorphous and fluorinedoped tin oxide coated glass substrates from a mixed solution of cuprous chloride, ferric chloride, stannic chloride and thiourea by simple and economical **Spray Pyrolysis Technique**. Structural, morphological,compositional, optical,electrical andthermo electrical properties of the deposited Cu_2FeSnS_4 thinfilms will be studied by using XRD, SEM, FESEM, TEM, EDAX, UV–Vis spectroscopy, DC electrical conductivity measurement and photoelectrochemical characterization technique.

1.Introduction:

Solar energy is regarded as one of the most promising renewable energies to support the sustainabledevelopment of human society. To utilize sunlight, three main problems should be solved:capture, conversion and storage. In photovoltaic cells, solar energy is converted into electrical energy. A photoelectrochemical (PEC) cell integrates capture and conversion in one step inexpensively.Thin film solar cells are based on semiconductor thin films.For lowering the fabrication cost of solar cells different types of semiconducting materials such as CdTe/CdSe, $Cu(In_xGa_{1-x})Se_2$ (CIGS), dye-sensitized TiO_2 and organic materials have been extensively studied. However due to limited availability of Indium and toxicity of cadmium inexpensive, non-toxic earth-abundant photovoltaic materials are of considerable interest.

Semiconductor material Cu_2ZnSnS_4(CZTS) has been studied as an alternative due to its optimal band gap (~1.5 eV) high absorption coefficient (~10^4 cm^{-1}) and having constituents of earth abundant elements. Photoelectric devices fabricated using (CZTS) have shown efficiencies as high as 7.2%. It has been observed that presence of Fe in place of Zn improves the efficiency of cell. As Fe is more soluble in lattice and increases the conductivity. Hence Cu_2FeSnS_4 (CFTS) semiconductor is considered to be one of the most promising materials. CFTS/CFTSe potentially cheaper and more cost effective alternatives to CIGS family. Their band gap lies between (0.9 to 1.5 eV) has high absorption coefficients (>10^4 cm^{-1}) which are beneficial for their use in solar cell applications.

2. Review of literature and development in the subject (Previous work done in the relevant area):

Xiayon Zhang [1]et al.havesynthesized Cu_2FeSnS_4 (CFTS) nanocrystals exhibiting a new wurtzite phase. They observed corresponding band gap of (CFTS) nanocrystals synthesized at different temperature varies between (1.49-1.54eV). The same group [2] also synthesized (CFTS) nanocrystals in the shape of oblate spheroid and triangular plate with band gap of 1.54±0.04 eVand 1.46±0.03 eV respectively by using solution based method. Xin Ziangand coworkers [3] synthesized C_2FeSnS_4 (CFTS) nanoparticles for application of as absorber layer in thin film solar cells by using convenient solvothermal method.Their study revealed that CFTS particle possesses pure tetragonal crystal structure with high crystallinity.

L. Zhu[4] et al. used a solvothermal method to synthesize Cu_2ZnSnS_4 (CZTS) and $Cu_2ZeSnSe_4$(CZTSe) nanoparticles CZTS/CZTSe binary film fabricated via layer by layer blade coating process on the fluorine doped tin oxide (FTO) substrates.They converted conventional dye-sensitized solar cells (DSSCS) in to double junction photoelectrochemical solar cell with replacement of Pt-coated counted as-prepared film as composite photocathodes compared with conventional DSSCs.The cell showedan increased short circuit current and power conversion efficiency.

HaoGaun[5] et al.synthesized Cu_2FeSnS_4 particles by using microwave irradiation method, XRD, SEM, TEM,UV-Vis-NIR absorbance spectroscopy measurements shows that the Cu_2FeSnS_4products exhibit flow-like particles with spherical structure has band gap (Eg = 1.52 eV) which indicates a potential candidate for application as a absorber layer in thin film solar cell. Krishnan Mukurala [6] et al.have synthesized compound of series $Cu_2ZnSnS_4$and Cu_2FeSnS_4 by thermal decomposition of metal precursors. The structural studies confirmed the formation of single phase.The morphology of CZTS and CFTS shows equiaxed nanoparticles ofapproximately 10-20 nm and 8-15 nm size, respectively. The obtainedoptical band gap of CZTS is 1.48 eV and for CFTS is 1.40 eV,thereby indicating the potential of CFTS for photovoltaic applications.

FarukOzel [7] et al. fabricated quaternary Cu_2FeSnS_4 (CFTS) nanocrystalline fibers through electrospinning techniques. Nanofibers showed well crystallization and tetragonal phase. The average diameters of fibers were found to be 100±50 nm. Cyclicvoltammograms showed that CFTS fibers having p-type nature. Rajiv RamanujamPrabhakar [8]and coworkers produced earth abundant Cu_2FeSnS_4 (CFTS) thin films by using spray pyrolysis of nontoxic aqueous precursors. Dhruba[9] et al. have

studied structural, optical and electrical properties of Cu_2FeSnX_4 (X: S, Se) thin film prepared by chemical spray pyrolysis. R Kondrotas[10] et al. investigatedselenization process of electrodeposited Cu-Zn-Sn precursor for $Cu_2ZnSnSe_4$ thin film solar cells.XiankuanMeng[11-12] et al. have studied two Cu based selenide semiconductors $Cu_2FeSnSe_4$ and$Cu(In, Al)Se_2$ (CIAS) fabricated using radio-frequency magnetron sputtering followed rapid thermal processing. Punarja Kevin et al.[13] used aerosol assisted chemical vapour deposition (AACVD) using mixture of $Cu_2FeSn(S_xSe_{1-x})_4$. S. Shalini [14] et al. had made review on natural dye sensitized solar cells along with various components.

3.Objectives of research/Proposed hypothesis:

Following are the objectives of present research work for the Ph.D. topic.

1)To synthesize good quality Cu_2FeSnS_4 thin films by chemical spray pyrolysis technique by optimizing various preparative parameters.

2)To characterize Cu_2FeSnS_4thin films for physical properties like structural,morphological, compositional,optical, electrical and thermoelectrical.

3)To study photoelectrochemical solar cell performance of Cu_2FeSnS_4 thin filmsdeposited on FTO coated glass substrates in various electrolytes.

4)To study the effect of film thickness on the properties of Cu_2FeSnS_4thin films.

4.Methodology to be adopted:

For the preparation of **Cu_2FeSnS_4 thin films** the **chemical spray pyrolysis**technique will be used amongst the many more such as chemical bath deposition method, electrochemical deposition, chemical vapour deposition, vacuum evaporation and Anodization.

Spray pyrolysis is a cheap and facile method for the preparation of quaternary chalcopyrite sulfidessuch as Cu_2FeSnS_4thin films. In this method, atomization provides a method to get droplets of precursor with very small sizes. As the droplets approach the substrate, the solvent vaporizes, the reactant diffuse to the substrate and a heterogeneous reaction occurs, which leads to the formation of thin films. In our present work, Cu_2FeSnS_4thin films will be prepared by chemical spray pyrolysis technique and properties of deposited films such as structural, morphological, compositional and optical characteristics characterized by XRD, SEM, FESEM, TEM, EDAX,UV–Vis and electrical properties will be studied. The Photo electrochemical properties of

Cu_2FeSnS_4thin films will be studied. Also the effect of film thickness on the properties of Cu_2FeSnS_4 thin films will be studied. The work will be divided in following manner:

a) Preparation of Good Quality Cu_2FeSnS_4Thin Films.

It is proposed to grow Cu_2FeSnS_4thin films by chemical spray pyrolysis. At initial stages the efforts will be done in order to deposit good quality Cu_2FeSnS_4thin films on glass and FTO coated conducting glass substrates. The various preparative parameters like concentration of precursor solution, thickness, substrate temperature and other parameters will be optimized to get good quality Cu_2FeSnS_4thin films. The as deposited films will be characterized by various characterization techniques.

b) Structural Studies:

The as deposited Cu_2FeSnS_4 thin films will be characterized by X-Ray diffraction (XRD) technique. The crystal structure, inter planar spacing, lattice planes, lattice parameters and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies:

The morphology of the prepared Cu_2FeSnS_4thin films will be studied by using Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM). The Grain Size, surface Roughness, Porosity will be studied using SEM and AFM techniques.

The Compositional Analysis of as deposited Cu_2FeSnS_4thin films will be studied by using Energy Dispersive Analysis by X–Rays (EDAX) technique. The correlation between as taken composition and film composition will be obtained.

d) Optical Studies:

The optical absorption of Cu_2FeSnS_4thin films will be obtained by using UV–Vis (UltraViolet–Visible) spectrophotometer. The coefficient of absorption, band gap energy (Eg), nature of transition, power factor will be obtained from optical absorption spectra.

e) Electrical and Thermoelectrical Studies:

The electrical conductivity measurements of as deposited Cu_2FeSnS_4thin films will be carried out by using DC two point probe method. The room temperature conductivity, activation energy will be obtained and correlated with film properties. The thermoelectric power measurement studies will be carried out in order to study the type of conductivity exhibited by Cu_2FeSnS_4thin films.

f) Photoelectrochemical Studies:

In order to find the applications of Cu_2FeSnS_4thin films, the Cu_2FeSnS_4 thin films deposited on FTO coated conducting glass substrates will be used as active photoelectrode in Photoelectrochemical (PEC) Solar Cells. The various cell parameters of

this PECsolar cells like Junction Identity Factor in Dark and under Illumination, Short Circuit Current, (Isc) Open Circuit Voltage (Voc), Fill Factor, Efficiency, Series Resistance and Shunt Resistance will be obtained.The PEC Cell will be studied for capacitance-voltage (C-V) characteristics, power output characteristics and spectral response characteristics.

g) Effect of Film Thickness:

In order to study the effect of technical parameters, the Cu_2FeSnS_4films with different thicknesses will be obtained and studied for all above mentioned characteristics.

5.Importance of the study/Society application:

The interests of Cu-based quaternary semiconductor materials and new approaches have recentlyattracted increased attention for the use of low-cost thin film solar cells. Cu_2FeSnS_4(CFTS)is a semiconductor best suited for solar energy conversion because of its good chemical and mechanical stability.Photovoltaic cells fabricated using CIGS family is more costly and due to limited availability of indium and gallium such solar cells becomes expensive. Semiconductor Cu-based quaternary Cu_2FeSnS_4(CFTS) is one of the most promising materials. It is more cheap and cost effective alternatives over CIGS family. Moreover, a deeper understanding on CFTS material also providesa strong background for cost effective band graded absorber layer of$Cu_2(Fe,Zn)SnS_4$ (CZFTS) alloyed chalcogenide alternative toband gap tuning with Ge alloyed CZTSSe absorber material for photovoltaic application.

As considering the above view, the properties of Cu_2FeSnS_4 thin films will be studied thoroughly in the present work for societal applications like solar cells.

6.Proposed work plan/ formulation and structure of study:

Plan of work and targets to be achieved during First Year:

A through literature survey and collection of papers will be done in order to get more and deep information about work already done and scope of present work. The literature includes collection of Journals, Books and some research papers related to the present work. Various chemicals will be procured and efforts will be done to deposit good quality Cu_2FeSnS_4thin films. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved duringSecondYear:

During second year, all preparative parameters will be optimized in order to get good photoactive Cu_2FeSnS_4thin films. All deposited films will be characterized by various techniques such as XRD, SEM, FESEM, TEM, EDAX, UV–Vis, DC electrical conductivity and photoelectrochemical technique. Also we will try to submit two or more research papers to reputed international research journals. Two progress reports will be submitted at the end of this year.

Plan of work and targets to be achieved duringThirdYear:

Results obtained in second year will be analyzed and published in reputed journals. Also the outcomes of our research work will be presented in national and international gatherings such as Seminars, Workshops, and Conferencesetcduring this year. Once this is done final synopsis will be submitted and after this thesis will be written. Thesis will be submitted to the university.

7. References:

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Place: Latur

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